We claim:

1. A process for the preparation of a fatty acid esters composition of a polyglycerine which comprises the reaction of a fatty acid with glycidol in the presence of a phosphoric acid-based acidic catalyst;

wherein said fatty acid is represented by general formula RCOOH, wherein R is an alkyl group, an alkenyl group, or a hydroxyl group-substituted alkyl group which have a carbon number ranging from 6 to 21.

- 2. The process as set forth in claim 1, wherein said R has a carbon number of at least 7.
- 3. The process as set forth in claim 1, wherein said phosphoric acid-based acidic catalyst is phosphoric acid or a phosphoric acid ester.
- 4. A process for the preparation of a highly-purified fatty acid esters composition of a polyglycerine comprising the steps:
 - (a) allowing a fatty acid to react with glycidol to obtain a fatty acid esters composition of a polyglycerine;
 - (b) removing water after adding water into said fatty acid esters composition of a polyglycerine, and then heating.
- 5. The process set forth in claim 4, wherein said fatty acid is allowed to react with glycidol in the presence of a phosphoric acid-based acidic catalyst.
- 6. The process set forth in claim 4, wherein said fatty acid is allowed to react with glycidol at a temperature ranging from 50 to 180°C.

7. The process set forth in claim 4, wherein water is added in the amount of 0.1 to 20% by weight based on said fatty acid monoester composition of a polyglycerine.